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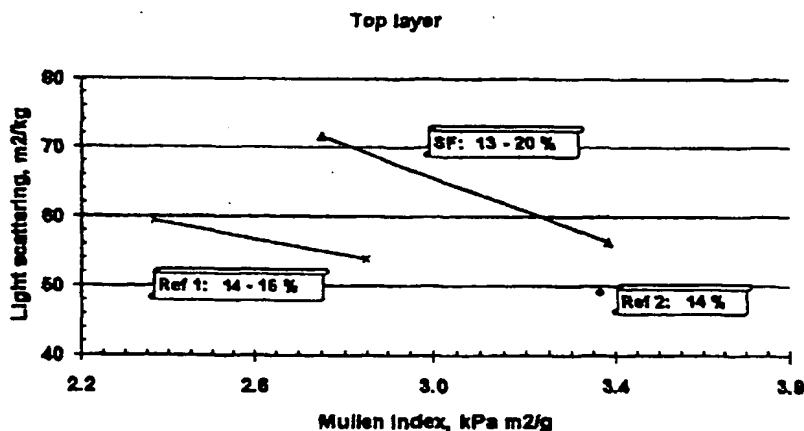
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(54) Title: **MULTILAYERED FIBROUS PRODUCT AND A PROCESS FOR THE PRODUCTION THEREOF**



(57) Abstract: The multi-layer fibrous product and a process for producing it. According to the present invention the fibre product comprises at least two overlapping fibre layers, whereby the one that forms the top layer of the product contains filler and is lighter than the layer under it and is at least essentially opaque. According to the present invention the filler of the top layer consists at least partially of cellulose or lignocellulose fibrils, on which light scattering material particles have been precipitated. The present invention can be used, for example, to produce white surface liner with a lighter top layer without impairment of the strength of the

surface. Thus, the grammage of the layer can be at least about 5% by weight less than a top layer, which has the corresponding opacity and formation, and which has been produced from the same fibre material and mineral pigments.

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Multilayered fibrous product and a process for the production thereof

The present invention concerns a multi-layer fibrous product according to the preamble of claim 1.

5

This kind of a product comprises at least two overlapping fibrous layers, of which at least the layer forming the operating surface of the product is light and essentially opaque (non-transparent), covering the fibre layer under it. The top layer contains filler and possibly conventional additives and auxiliary agents for paper.

10

The present invention relates also to a process according to claim 12 for producing of multi-layer fibrous product.

A multilayered fibrous product usually consisting of two or three layer is called a "liner".

15

A liner can be completely brown (kraft-liner) or partially white (white-lined liner) or its top layer can be coated. The liner can be made of virgin fibre or recycled fibre or both.

20

A liner is used as a surface of a background liner in a corrugate board package. The special characteristics of kraft-liners are strength, uniform quality and product safety. Strength is with kraft-liners a very important competitive advantage when comparing with recycled fibre-based products. The advantages of using test liners that contain recycled fibre are low price and the ecological values that support recycling.

25

The products called "Kemiart Graph" and "Kemiart Lite" and the uncoated "Kemiart Brite" of Oy Metsä-Botnia Ab can be mentioned as examples of commercial coated liners. The liner product of Oy Metsä-Botnia Ab is a kraft-liner that has two fibre layers, the base layer being high yield softwood sulphate pulp and the top layer of bleached birch and softwood sulphate pulp. The fillers are used in the top layer to give the surface more brightness and smoothness, which improves the printability properties. Other chemicals, such as retention agents, are also used in production of liner, in order to retain the noil material and filling agents in the product instead of cycling it in the water cycle, and AKD adhesives to improve water resistance. The coating is added to the coated products with an on-line coating unit. The coating is, for example, a combination of kaolin, carbonate and

30

latex which improves significantly the printability of the product. The final gloss and smoothness of the final product are obtained with calendering.

5 The method of producing the top layer of the white lined linerboard (cover layer) is considerably more expensive than the method of producing brown back layer. The product can be optimised by changing, for example, the strengths of the fibre layers. In that case it would be reasonable to produce the liner the top layer of which is as lightweight as possible. So far, however, the attempts to reduce the weight of the cover while maintaining a sufficient brightness of a liner without making the cover too weak, have been
10 unsuccessful.. The amount of the white fibre cannot be decreased easily, without the brown fibre showing through.

The top layer does also need to have a good formation, which shows directly as good printability. Thus bad formation is visible especially well in grey scales of offset printing
15 and as mottled print quality.

It is an object of the present invention to eliminate the problems involved with the known methods and to provide a novel solution for producing multi-layer fibre products, such as liners.
20

The present invention is based on the idea that a composite filler consisting of fibrils and mineral pigments is used as a filler of the top layer of the fibre product mentioned in the introduction.

25 Finnish Patent Specification No. 100729 discloses a papermaking filler comprising porous aggregates formed by precipitated calcium carbonate particles on the surface of fines. What characterises this new kind of filler is that, according to the patent specification, the calcium carbonate is precipitated on fine fibrils produced by refining cellulose fibres and/or mechanical pulp fibres. The size distribution of the fines fraction corresponds
30 mainly to the wire screen fraction P100.

According to the present invention, it has been found that when the top layer of a multi-layer product is filled with the filler described above, the opacity of the surface increases so drastically that the grammage of the cover can be reduced significantly. The top layer

containing the new filler covers very efficiently the brown background despite the lower grammage.

Furthermore, within the scope of the present invention it has been found that also other
5 similar fillers consisting at least partly of cellulose or lignocellulose fibrils, over which
light scattering material particles has been precipitated, can be used as fillers. These
particles are typically inorganic salts precipitating in an aqueous phase, such as calcium
carbonate, calcium sulphate, barium sulphate and calcium oxalate.

10 According to the present invention it is, thus, possible to reduce the thickness of the multi-
layer paper without impairing the opacity by using a filler that comprises fibrils over which
calcium carbonate has been precipitated. GB Patent No. 628603 describes a multi-layer
paper or board, the top layer of which contains modified fibre bulk. The bulk has been
produced by impregnating the pulp with calcium chloride, after which the manipulated
15 bulk is put in contact with carbonate compound, which causes the calcium carbonate to
precipitate on the fibres – not on the fibrils. In the case corresponding to that described in
the GB Patent, the bulk has considerably poor strength properties. It is stated in the
publication, that it would not be possible to produce paper from this material. Moreover,
the bulk has very poor retention.

20 More specifically, the fibre product according to the present invention is mainly
characterised by what is stated in the characterising part of the claim 1.

The process according to the present invention, for its part, is characterised by what is
25 stated in the characterising part of claim 12.

The present invention provides considerable advantages. Thus, a white lined liner can be
prepared with a lighter top layer without compromising the strength of the surface. With
the help of a new kind of a composite filling agent, the proportions of the white and brown
30 layers can be changed much more easily. As the filler content can be increased and as the
filler is extremely white, the amount of the white layer can be significantly decreased. By
decreasing the white fibre layer, the commercial manufactures of liners can also decrease
the total grammage of the liner. For example, it should be mentioned, that the grammage
of the top layer according to the present invention can be at least about 5 % by weight,

preferably at least 10 % by weight smaller than a top layer that has a corresponding opacity and formation and is prepared from the same fibre material and mineral pigment.

5 The filler has been found to improve the formation and stiffness of the top layer. The filler described in the FI Patent Specification No. 100729, referred hereinafter with its product name "SuperFill", retains well, which makes it possible to reduce the dosage of retention agents and still maintain a purer process. The better retention helps also to optimise/decrease the dosage of other paper making additives. Purity helps the operation of the machine and generally the operation efficiency of the machine improves, as the
10 frequency of breaking down is smaller.

The present invention will be examined below in greater detail with the help of a detailed description and some examples.

15 Figure 1 present a side view of the principal structure of a two-layer fibre product and Figure 1b the corresponding four-layer fibre product,
Figure 2 shows the light scattering factor of a two-layer fibre product produced according to the present invention and two reference products as a function of the Mullen indices with two different filling factors,
20 Figure 3 shows corresponding results as a function of the bonding power (ScottBond), Figure 4 shows corresponding results as a function of the tensile index, and
The figure 5 uses bar graphs to present the brightness of four two-layer fibre products, wherein two has top layers that contain filler according to the present invention, and two other contain reference filler.

25

Filler and its preparation

As stated above, according to the present invention, composite filler comprising cellulose fibrils, on which light scattering pigments have been precipitated, is added as filler to the
30 top layer of the multi-layer fibre product. Fibrils can originate from chemical pulp or mechanical pulp or mixtures thereof. By chemical pulp reference is herein made to a pulp, which has been treated with cooking chemicals to delignify cellulose fibres. According to a preferred embodiment the fibrils are obtained by refining pulps produced with the sulphate

process or with some other alkaline cooking method. In addition to chemical pulps, fibrils can originate also from chemi-mechanical or mechanical pulps.

Typically, the average thickness of cellulose or lignocellulose fibrils is smaller than 5 μm , conventionally smaller than 1 μm . The fibrils are characterized by at least one of the following criteria:

- a. they correspond to a fraction which passes a 100-mesh screen; and
 - b. their average thickness is 0.01 – 10 μm (preferably at maximum 5 μm and in particular at maximum 1 μm) and their average length is 10 – 1500 μm .
- 10 The source material for the fibrils, i.e. the fines based on cellulose or other fibers, is fibrillated by beating it in a pulp refiner. The desired fraction may, when necessary, be separated by using a screen, but fines need not always be screened. Suitable fibril fractions include wire screen fractions P50 – P400. Preferably refiners with grooved blades are used.

The light-scattering material particles in the filler are inorganic or organic salts that can be formed from their source materials by precipitation in an aqueous medium. Such compounds include calcium carbonate, calcium oxalate, calcium sulphate, barium sulphate, and mixtures thereof. The material particles are deposited on the fibrils. The amount of an inorganic salt compound in proportion to the fibril amount is approx. 0.0001 – 95 % by weight, preferably approx. 0.1 – 90 % by weight, most suitably approx. 60 – 80 % by weight, calculated from the amount of filler, and approx. 0.1 – 80 % by weight, preferably approx. 0.5 – 50 % by weight, of the paper.

In the following, the present invention is examined with particular reference to a product according to FI Patent Specification No. 100729, but it is clear that the present invention can be adapted for other products mentioned hereinbefore by changing appropriately the source materials of the light scattering pigment.

The filler is produced by precipitating a mineral pigment on the surface of fine fibrils prepared from cellulose fibres and/or mechanical pulp fibres. For example, the precipitation of calcium carbonate can be carried out by feeding into an aqueous slush of fibrils an aqueous calcium hydroxide solution which possibly contains a solid calcium hydroxide, and a compound which contains carbonate ions and is at least partly dissolved

in water (e.g. sodium carbonate or ammonium carbonate). It is also possible to introduce into the aqueous phase carbon dioxide gas that, in the presence of calcium hydroxide, produces calcium carbonate. There are formed string-of-pearls-like calcium carbonate crystal aggregates, which are held together by fibrils, i.e. fine strands, and in which the calcium carbonate particles are deposited onto the fine fibrils and attached to them. The fine fibrils together with calcium carbonate form string-of-pearls-like strands, and the calcium carbonate aggregates primarily resemble strings of pearls in a pile. In water (slush) the ratio of the effective volume of the aggregates to the pulp is very high compared with the corresponding ratio of conventional calcium carbonate used as filler. By "effective volume" is meant, in this case, the volume required by the pigment.

The diameter of the calcium carbonate particles in the aggregates is about 0.1 to 5 μm , typically about 0.2 to 3 μm . In particular, the fibrils correspond (at least to 55 %) to wire screen fractions P50 to P400.

1 to 90 % by weight (dry weight), typically about 5 to 50 % by weight, of this kind of filler is added to the top layer of a multi-layer product. Usually the filler described forms at least 5 % by weight, most suitably from 10 to 100 % by weight of the filler of the bottom web and respectively 10 to 50 % by weight of the fibre material of the bottom web. In principle it is also possible to produce a bottom web the fibre material of which consist totally of fibrils of the filler, so, in general, the present filler can form 1 to 100 % by weight of fibre material of the bottom web.

In the slush used in the production of the bottom web, part of the filler can consist of conventional fillers, such as calcium carbonate. However, preferably at least 80 %, especially preferably at least 90 % of the precipitated light scattering pigment particles are attached into the fibrils.

Multi-layer structure

Figures 1a and 1b illustrate the structures of the multi-layer products containing two and four layers, respectively. Figure 1a illustrates a typical white lined liner board and Figure 1b illustrates so called test liner.

The grammage of the fibre product according to the present invention is preferably about 50 to 500 g/m², typically about 80 to 350 g/m². Usually its grammage is over 125 g/m², but products having a grammage below 100 g/m² qualify for small packages.

5

Preferably the liner according to the present invention comprises a two-layer product (see Figure 1a), that has a surface of a cover layer 1 and a back layer 2. The top layer covers the back layer so that the back layer cannot be seen through the top layer.

- 10 It is also possible to produce three-layer or four-layer products. In principle the number of layers in a layer product has no upper limit, there can be even up to 5, 6 or 7 layers. What is essential in the present invention, is that the top layer contains filler described more precisely hereinbefore, so that the top layer covers the layers under it, the layers that can be produced from raw materials of cheap costs.

15

Among multi-layer products, the test liner type four-layer products of Figure 1b, having a top layer 3, a layer 4 under the top layer, intermediate layer 5 and a back layer 6, are to be mentioned.

- 20 Different raw materials can be used for production of a fibre product according to the purpose of use. Both virgin fibres and recycled fibres can be used. The virgin fibre can originate from softwood or hardwood (wood chips) or it can originate from cuttings. Especially preferably virgin pulp is used in the top layer. This is most suitably produced by sulphate cooking (kraft pulp), because sulphate cooking gives a mass having especially
- 25 good strength properties, as the name suggests. The recycled fibre can originate e.g. from used corrugated board packages (OCC) or mixed fibres. Recycled fibres are used especially for the production of test liners. The surface and back layer(s) can be produced from similar raw materials or from different source fibres. If virgin fibre, such as kraft pulp, is used for both, then the mass of the back layer can be cooked in high yield, after
- 30 which a mild refining is performed on it. Mass that has been cooked to a lower kappa and also refined more than mass of the back layer, is used for the top layer. Typically the pulp of the back layer is cooked to a kappa value of 30 to 70 and the pulp of the top layer to lower kappa value of 25 (the kappa number of the unbleached pulp). Bleaching can be performed in a manner known per se, e.g. as ECF or TCF bleaching.

Retention agents can be added to the slush e.g. in about 0.5 to 3 % of the amount of the fibre material. However, it has been found in connection with the present invention that the filler described here gives such a good retention that no retention agents are needed for the layer the and amount of the retention agents can be significantly decreased. The liner is stuff or surface sized to improve the moisture resistance. If a low quality recycled fibre is used as raw material, it is preferable to use a surface-size press to produce a product that has sufficient strength. According to the machine the distribution of the base weight between the top and the back layer is about 20/80...40/60, typically about 30/70. Thus the grammage of the top layer is generally about 20 to 125 g/m² (see below). When operating according to the present invention, the grammage of the top layer can be decreased over 10 %, up to 20 % or more, without deteriorating the optical or mechanical properties of the cover.

The layer product is produced in a manner known per se. According to one preferred embodiment both or all layers are produced first from slush of their own and spread on the Fourdriner wire. After this, the layers are couched fastened into each other. With regard to the production process, a reference is made to a text by Ari Kiviranta "Board Grades", in a book series Paper Making Science and Technology, Book 18, Paper and Board Grades, Fapet Oy, Jyväskylä 2000, pages 68 and 69.

A planar fibre product according to the present invention can be used as a top layer of different corrugate board packages. The solution according to the present invention is especially preferably suitable for white lined top liner and coated white lined liner, both of which are used for demanding printing works. In these objects the fact that the surface of the liner according to the invention is extremely smooth and uniform, and has at the same time high opacity and brightness can be made use of. Generally the grammage of the top layer is about 20 to 125 g/m², most suitably about 50 to 80 g/m², especially preferably about 55 to 70 g/m², and bleached chemical cellulose pulp is used of the top layer. In order to obtain a very good formation in the preferred embodiment of the present invention, mainly hardwood is used in the top layer. Thus e.g. over 60 % by weight, typically over 80 % of fibre material of pulp is hardwood and the rest softwood. The fibre material of pulp can consist totally of hardwood.

Conventional coating mixtures can be used for coating of the coated white lined top layer product. Precipitated calcium carbonate, ground calcium carbonate, calcium sulphate, calcium oxalate, aluminium silicate, kaolin (hydrous aluminium silicate), aluminium hydroxide, magnesium silicate, talc (hydrous magnesium silicate), titanium dioxide and barium sulphate, and mixtures thereof can be used as pigments. Synthetic pigments can also be used. Of the pigments mentioned above, the main pigments are kaolin, calcium carbonate, precipitated calcium carbonate and gypsum, which in general constitute over 50 % of the dry solids in the coating mix. Calcined kaolin, titanium dioxide, satin white, aluminium hydroxide, sodium silicoaluminate and plastics pigments are additional pigments, and their amounts are in general less than 25 % of the dry solids in the mix. Special-quality kaolins and calcium carbonates, as well as barium sulphate and zinc oxide of the special pigments should be mentioned as examples.

Any known binders generally used in paper production can be used as binders in the coating composition. Besides the individual binders, it is also possible to use mixtures of binders. Examples of typical binders include synthetic latexes made up of polymers or copolymers of ethylenically unsaturated compounds, e.g. copolymers of the butadienestyrene type, and polyvinyl acetate having comonomers that contain carboxyl groups. Together with the materials mentioned above, it is possible to use, for example, water-soluble polymers, starch, CMC, hydroxyethyl cellulose and polyvinyl alcohol as binders. Furthermore, conventional additives and auxiliary agents, such as dispersants, agents affecting the viscosity and water retention of the mix, lubricants, hardeners used for improving water-resistance, optical auxiliary agents, anti-foaming agents, pH control agents, and preservatives can be used in the coating composition.

The coating mix can be applied to the material web in a manner known per se. The coating can be done before couching. Preferably it is done after forming the multi-layer structure. The method according to the present invention for coating paper and/or board can be carried out with a conventional coating apparatus, in other words by blade coating, or by film coating or JET application. Coating can be done on-line or off-line.

The amount of grammage of the coating layer varies from 5 to 30 g/m².

It has also been found in the context of the the present invention, quite surprisingly, that the above-described filler does not only improve opacity of the top layer but the filled layer is also very easy to be coated. The amount of pigment or amounts of coatings required for the desired brightness can be decreased with the filler.

5

According to the present invention, the opacity is significantly improved with the filler.

The following non-restrictive examples illustrate the present invention. The measurement results indicated for the paper properties in the examples have been determined by the following standard methods:

10

Surface roughness: SCAN-P76:95

Porosity: SCAN-P60

Resistance of air permeability: SCAN-M8,P19

15

Example 1

Production of filler

Refining of chemical pulp

20

Birch sulphate pulp was refined with a Valmet JC-01 refiner to produce pulp that is suitable for production of filler. The consistency of refining was about 4 % and the total energy consumption was 343 kWh/t and specific edge load was 0.5 J/m.

25 Properties of the product are presented in Table 1.

Table 1. Fibre properties before and after refining

	Before refining	After refining
Fibre length (length), mm	0.86	0.58
Fibre length (weight), mm	1.00	0.77
SR°	16	86

Carbonating of pulp

Carbonating was performed in tap water according to the FI Patent Specification No. 100729. Water slurry that has dry matter content of 2.22 % was produced. The final
5 product had CaCO_3 content of 69.7 % and a specific surface area of $10.6 \text{ m}^2/\text{kg}$.

Example 2

10 Fibre layers suitable for cover layer of two-layer white lined liner was produced from chemical pulp that contained 70 % by weight of birch pulp and 30 % by weight of pine pulp. Filler was added from the pulp in the slush in various amounts: 13 and 20 % by weight, respectively, of filler described in example 1 (SuperFill), 14 and 16 % by weight, respectively, precipitated calcium carbonate (PCC, Albacar LO, ref. 1) and 14 % by weight of mixture of chalk and calcined kaolin (ref. 2).

15

Figures 2 to 4 illustrate the light scattering ability of the obtained fibre layers as a function of mechanical strength properties. The figures show that the light scattering factor is at least 25 % and about 20 % greater with the SuperFill filler when compared with references 1 and 2 in constant strengths.

20

Consequence of this is that the grammage of the surface can be decreased by about 20 %, which decreases significantly production costs of liner.

25

Figure 5 shows a result in which the above presented results are substantiated. The result is from a liner test run made by pilot machine (FEX) of STFI in Stockholm, wherein the grammage of the surface was decreased from the normal level of 75 g/m^2 to a level of 65 g/m^2 . A two-layer fibre structure was produced for the test. The ISO brightness of the product was determined.

30

Figure 5 shows that the top layer lightened 10 g/m^2 with Superfill, generates brightness which is 4 brightness units greater as compared with the reference 2, in which the grammage is 75 g/m^2 . The result is extremely good and it suggests that the grammage of the surface can be decreased even lower than 10 g/m^2 .

Claims:

1. A multi-layer fibrous product comprising of at least two overlapping fibre layers (1, 2; 3-6), of which the one (1; 3), which forms the top layer, contains filler and is lighter than the layer under it (2; 4-6) and it is at least essentially opaque, characterized in that the filler of the top layer (1; 3) consists at least partially of cellulose or lignocellulose fibrils, on which light scattering material particles have been precipitated.
2. A fibrous product according to claim 1, characterized in that the filler comprises cellulose or lignocellulose fibrils produced by refining and screening from plant fibres, the average thickness of which is less than 5 μm .
3. A fibrous product according to claim 2, characterized in that the light scattering material particles has been precipitated over fibrils corresponding to a fraction that passes through a 50 mesh screen and/or having an average thickness of 0.01 to 5 μm and an average length of 10 to 1500 μm .
4. A fibrous product according to any of claims 1 to 3, characterized in that the light scattering material particles are inorganic salts that can be formed from their source materials by precipitating in an aqueous medium.
5. A fibrous product according to claim 4, characterized in that the light scattering material particles are calcium carbonate, calcium oxalate, calcium sulphate, barium sulphate or mixtures thereof.
6. A fibrous product according to any of the preceding claims, characterized in that it comprises white lined top liner or coated white lined liner.
7. A fibrous product according to any of the preceding claims, characterized in that its grammage is preferably about 50 to 500 g/m^2 , typically about 80 to 350 g/m^2 , in which case the grammage of the top layer is about 20 to 125 g/m^2 , preferably about 50 to 70 g/m^2 .

8. A fibrous product according to any of the preceding claims, characterised in that the distribution of the grammage between the top and back layers are between about 20/80...40/60.
- 5 9. A fibrous product according to any of the preceding claims, characterised in that the top layer (1; 3) is produced from chemical cellulose pulp comprising hardwood pulp, softwood pulp or a mixture thereof.
- 10 10. A fibrous product according to any of the preceding claims, characterised in that the back layer comprises 1 to 5 layers (2; 4-6) that have been produced from virgin fibre or recycled fibre.
- 15 11. A fibrous product according to any of the preceding claims, characterised in that the grammage of the top layer is at least about 5 % by weight, preferably at least 10 % by weight, less than the top layer that has been produced from the same fibre material and mineral pigments and that has corresponding opacity and formation.
- 20 12. A process for producing a multi-layer product, according to which process a filler-containing fibre layer, which forms the surface (1; 3) of the fibre product and covers the back layer, is fitted on top of a backing layer (2; 4-6) that consists of at least of one fibrous layer, characterised in that the top layer (1; 3) is formed from slush of fibre material, to which a product comprising cellulose or lignocellulose fibrils, on which light scattering material particles have been precipitated, is added as a filler.
- 25 13. A process according to claim 12, characterised by using a filler that comprises cellulose or lignocellulose fibrils produced from plant fibres by refining and screening, having an average thickness of less than 5 μm .
- 30 14. A process according to claim 13, characterised by using a filler, in which the light scattering material particles have been precipitated on fibrils corresponding to a fraction that passes through a 50 mesh screen and/or having an average thickness of 0.1 to 10 μm and an average length of 10 to 1500 μm .

15. A process according to any of claims 12 to 14, characterised by using a filler in which at least 80 % of the precipitated light scattering pigment particles are attached to the fibrils.
- 5 16. A process according to any of the claims 12 to 15, characterised in that the top layer is coated in a paper machine with a pigment-containing coating mixture.
17. A method according to any of claims 12 to 16, characterised in that the top layer (1; 3) and the back layer(s) (2; 4-6) are formed separately on the Fourdriner wire and
10 couched when still wet.

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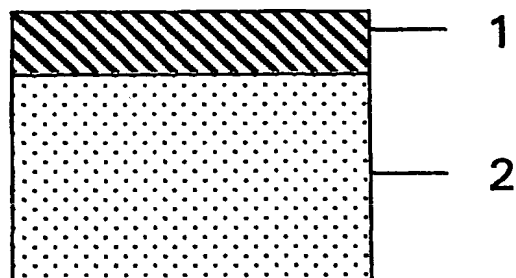


Fig. 1a

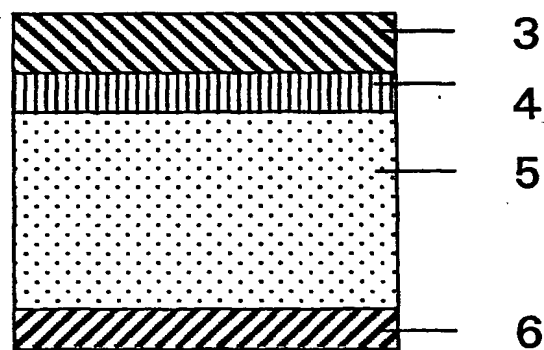


Fig. 1b

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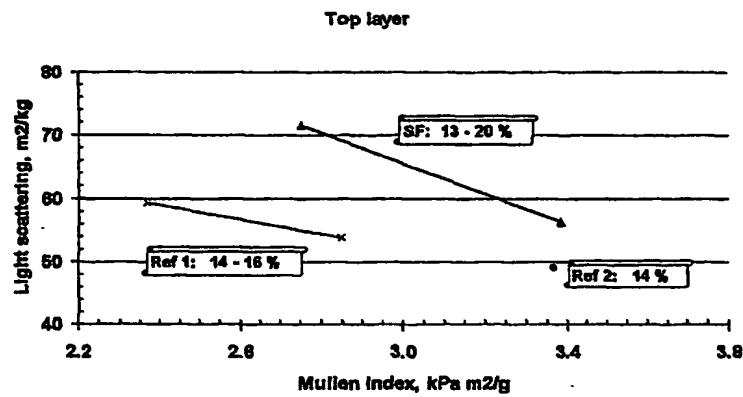


Fig. 2

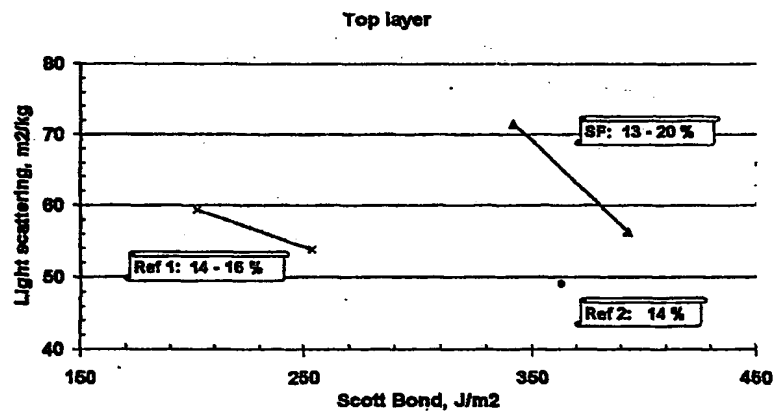


Fig. 3

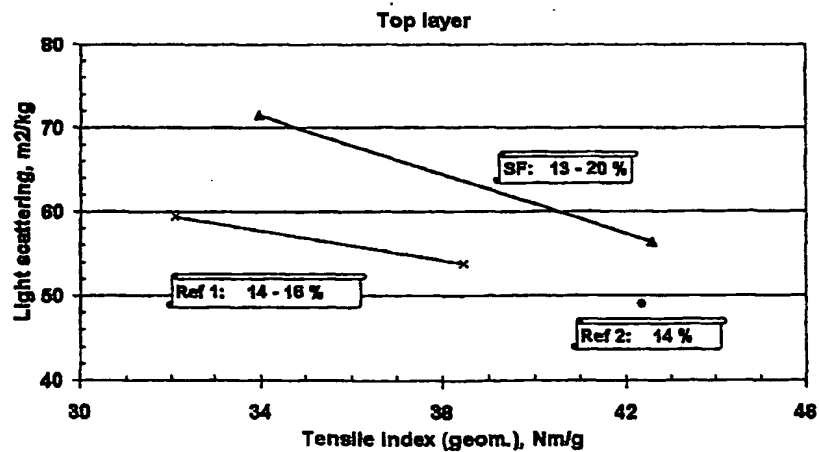


Fig. 4

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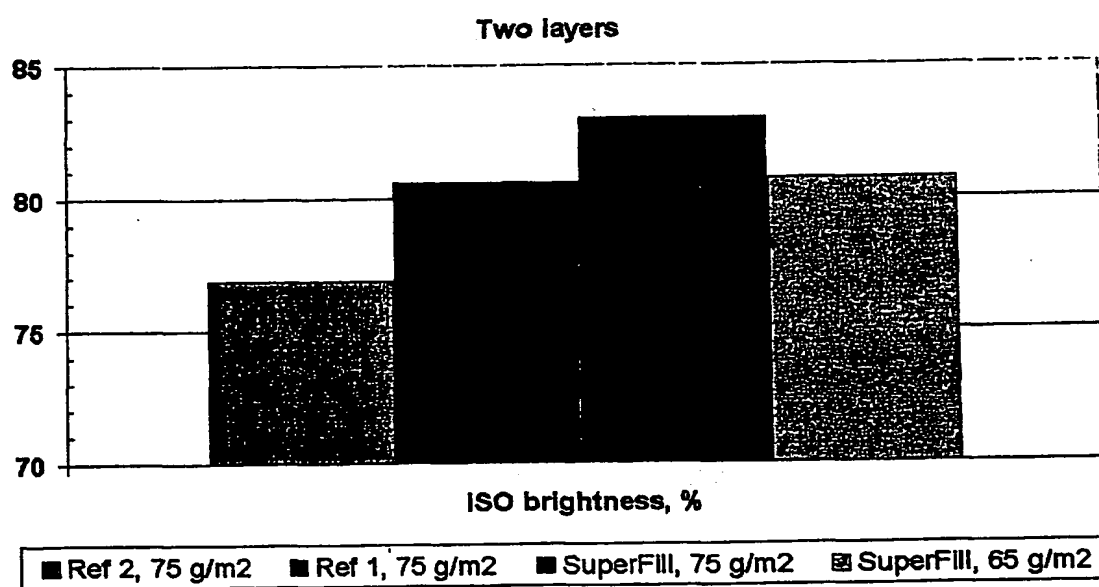


Fig. 5

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 02/00342

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: D21H 17/69, D21H 27/38

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI, EPODOC, PAPERCHEM

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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